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In-situ Differential Reflectance Study of the Etching of  $\text{SiO}_2$  Films

by

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# IN-SITU DIFFERENTIAL REFLECTANCE STUDY OF THE ETCHING OF SiO<sub>2</sub> FILMS

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## Abstract

A differential reflectance technique has been applied to study the etching of SiO<sub>2</sub> films on Si substrates in-situ in the liquid (HF/H<sub>2</sub>O) environment as well as ex-situ. Essentially, the technique scans an incident optical beam in the spectral range of 200-800 nm across two adjacent samples at near normal incidence and the reflected beams are detected using lock-in amplification so as to measure only the difference in the reflectance spectra. This study demonstrates the great sensitivity of the technique to follow the etching experiment in-situ, and in conjunction with simulated spectra and ex-situ results, a new spectral feature is seen which may be evidence for an electric double layer at the Si surface in the etch solution.



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## Introduction

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In microelectronics processing, the cleaning of silicon substrates prior to processing and the etching of  $\text{SiO}_2$  films on Si for various lithographic procedures often involves the use of aqueous HF solutions. Previous studies<sup>(1,2)</sup> have shown that the use of HF alters the Si surface and the oxidation kinetics. More recent studies<sup>(3,4)</sup> have confirmed these results and indicate that the major effect is at the Si surface. Studies aimed at the elucidation of the specific role of HF and other typical cleaning and etching media such as  $\text{NH}_4\text{OH}$  have employed such in-situ techniques as ellipsometry and contact angle measurements in the etching solutions during the processing<sup>(5,6)</sup>. From these studies, the HF in solution has been observed to cause the formation of a hydrophobic film on Si which is absent in  $\text{NH}_4\text{OH}$  solutions. The film is likely a hydrocarbon or fluorocarbon film. Some recent studies have shown only the appearance of H at the Si surface<sup>(7,8)</sup> although F and other impurities have also been reported<sup>(9)</sup>. From these studies the specific nature and role of the etching solutions has been elucidated but not fully characterized. For example, it is now clear that HF solutions modify the Si surface, but the nature of the modification, the specific role of the modification on subsequent processing steps, the change of barrier height, interface states and charge are all open questions. For resolution of these detailed and basic issues more incisive experimental results are needed. It is preferable that the experiments be performed in-situ in the processing media, so as to avoid the ambiguity of other ambients and even vacuum conditions on the treated surface. To this end the present study reports on the use of differential reflectance, DR, techniques to study the HF solution etching of  $\text{SiO}_2$  on Si. The technique can be

employed both in-situ and ex-situ and is found to be extremely sensitive. Using one version of DR techniques in which different samples to be compared with respect to reflectivity are placed side by side and sequentially scanned, it was shown(10-12) that differential reflectometry is very sensitive to the small changes in both composition of alloys and damage caused by ion bombardment on the surface of a Si sample. The differential nature of the technique cancels out effects of experimental environment such as the solution in an in-situ solution measurement thereby rendering the measurement sensitive only to the change of the sample. Other versions of DR techniques compare different spectra of the same sample before and during surface treatments(13), however, we do not use that technique here and we will not consider it further.

### **Experimental Procedures**

The details of the DR technique used in the present study, as well as experimental studies have been reported (see for example references 10-12) and are briefly discussed below. Essentially, the technique is a type of reflectance modulation spectroscopy in which both chemical and physical changes made to a surface are sensitively detected relative to an adjacent reference. The measurement of optical reflectance is performed near normal incidence using a rapidly rastered beam incident upon two adjacent samples which are subtly different in composition or surface condition. The detected reflected light is measured with the use of lock-in amplification tuned to the rastering frequency thus only the difference,  $\Delta R$ , between the two samples is obtained.

The normalized difference of the intensity of the reflected light,  $(\Delta R)/R$ , from two adjacent samples is measured as a function of wavelength from 250 nm to 750 nm. The differential reflectance is defined as follows:

$$\frac{\Delta R}{R} = \frac{R_1 - R_2}{(R_1 + R_2)/2} \quad (1)$$

where  $R_1$  and  $R_2$  are the reflectance of sample 1 and sample 2, respectively.

Figure 1 shows a block diagram of the apparatus. The 600 W Xe-high pressure arc lamp is used as a wide band light source in the visible to near uv spectral range that is scanned in wavelength using a monochromator. The light from the monochromator is focused onto the samples at near normal incidence by a focusing lens. A galvanometric optical scanner is placed between the samples and the focusing lens, in order to raster the incident beam equally over two samples. The frequency of the scanner is variable, but we used 250 Hz so as to be above usual interferences. The reflected beam from the samples is collected and focused onto a photomultiplier tube by a concave mirror. A uv-grade diffuser is placed in front of the photodetector to avoid an effect due to the inhomogeneous response of the detecting surface. The signal from the photomultiplier tube is simultaneously fed into a lock-in amplifier and a low-pass filter. Thus, both the difference,  $\Delta R$ , and average,  $R$ , of the signal which is proportional to the difference and average of the reflectivities from two samples, respectively, are measured. The ratio,  $\Delta R/R$ , is obtained by a dividing circuit in the lock-in amplifier, and stored on a small computer for further analysis. The wavelength of the incident light is automatically controlled by a stepping motor driver also using a personal computer. All optics

are enclosed within a light proof box to shield from laboratory light. It should be noticed that any environmental chamber can be used to house the samples providing the samples can be scanned, the reflected light can be detected, and the light path does not alter the beams except for that from the samples.

Commercially obtained device quality silicon wafers of (100) and (111) orientations, both n and p type in the 2 ohm cm resistivity range were cleaned by following a slightly modified RCA cleaning procedures prior to oxidation(14). The samples were thermally oxidized in a fused silica tube furnace in clean dry oxygen which yields MOS quality  $\text{SiO}_2$  films on Si. After oxidation a sample is cleaved into two pieces having straight and sharp sides. Before each experiment, the optics are aligned and calibrated by using two identical samples to yield a null background of  $\Delta R/R$ . With properly aligned optics, it is routine to obtain a background spectra within  $\pm 0.2\%$  and without any spectral features.

Both ex-situ and in-situ experiments have been performed to study etching of  $\text{SiO}_2$  films in  $\text{HF-H}_2\text{O}$  solutions. For ex-situ experiments, after the desired processing, two samples are mounted vertically side by side in room ambient on the sample holder. For the experiments reported below we started with two samples of equal film thickness, and then one of the samples was etched by dipping in a dilute HF solution of about 450 parts deionized water to one part HF(49% by volume), rinsed in deionized water, and dried by nitrogen gas. The thickness of the  $\text{SiO}_2$  film was measured by ellipsometry. Then, the sample was remounted along side the unetched sample and  $\Delta R/R$  spectrum was obtained. The procedure was repeated until the etched sample was bare Si with only a native oxide.

For in-situ experiments, two Si substrates, each with different  $\text{SiO}_2$  film thicknesses, are mounted on a teflon sample holder and placed in a fused silica sample cell. The sample cell has an optical window perpendicular (a deviation from perpendicular is best to avoid reflections from the window) to the optical axis of the incident beam, and the cell has an inlet and outlet so as to permit the addition of etchant or change the solution without otherwise interrupting the experiment or exposing the samples to the laboratory ambient. With the samples in the cell containing 16-18 Mohm deionized water, the background spectra are obtained. Subsequently, HF solution is introduced so as to attain the desired concentration of the HF etching solution. The differential reflectance spectra are obtained as a function of exposure time in the solutions, in order to follow the etching process. Essentially, the in-situ DR experiment observes two  $\text{SiO}_2$  films etching simultaneously. However, the two films are initially of unequal thickness, hence the interface will be reached for one sample sooner than for the other. In the experiment, the differences are recorded during etching and finally with both Si substrates bare.

Using a simple optical model of a homogenous film on a planar substrate surface, classical electromagnetic theory permits a simulation of the reflectance spectra based on literature values for the optical properties of the film and substrate in the wavelength range studied. Hence, a comparison of theory and experiment will provide information relative to the assumptions in the model. The ex-situ and in-situ experimental results along with simulations of the experiments will be shown below.



## Results and Discussion

### Simulations

The reflectance of a Si substrate covered with a SiO<sub>2</sub> film is calculated using the complex-amplitude reflection coefficient,  $r$ , for the ambient-film-substrate system given as(15):

$$r = \frac{r_{01} + r_{12}\exp(-j2\beta)}{1 + r_{01}r_{12}\exp(-j2\beta)}$$

$$\beta = 2\pi(d/\lambda)N_f \quad (2)$$

where subscripts 0, 1, and 2 represent ambient, film, and substrate, respectively.  $r_{01}$  and  $r_{12}$  represent the Fresnel reflection coefficients at the ambient-film and film-substrate interface, respectively.  $d$  is the film thickness,  $\lambda$  is the wavelength of the incident light, and  $N_f$  is the complex refractive index of the film.  $r_{01}$  and  $r_{12}$  are functions of the complex refractive index of the ambient, film, and substrate. Equation 2 includes the multiple reflections of the incident light in the film.  $\beta$  is the phase change experienced by the multiply-reflected waves inside the film on a single traverse between boundaries. Reflectance,  $R$ , is calculated from the product:

$$R = rr^* \quad (3)$$

where  $r^*$  is the complex conjugate of  $r$ . In the simulation, the subscripts 0, 1, and 2 represent air, SiO<sub>2</sub>, and silicon substrate, respectively. Optical constants of SiO<sub>2</sub> and Si were found in the literature(16).

Figure 2 shows the simulated reflection spectra as a function of wavelength for different thickness of SiO<sub>2</sub>, and the spectrum corresponding to zero thickness of SiO<sub>2</sub> is the reflection

spectrum of the bare silicon. All the simulated spectra have two major peaks at around 275 nm and 365 nm in the 250 nm to 800 nm spectral range which is experimentally scanned. These two peaks are due to the interband transitions in bulk silicon, viz.  $L'_3 \rightarrow L_1$  (3.4 eV) and  $\Sigma$  (4.2 eV), and there is a small peak at 225 nm (5.6 eV) which is due to  $L'_3 \rightarrow L_3$ , but which is on the borderline of detection in the present experiment(12). In the wavelength range investigated  $\text{SiO}_2$  is transparent, hence the effect of the presence of the  $\text{SiO}_2$  film on silicon substrate is merely to decrease the overall reflectivity via interference, but not to change the main features of the reflection spectrum due to Si. The reflectivity decrease is due to the interference between the incident light reflected from the top surface of  $\text{SiO}_2$  and from the  $\text{SiO}_2$ -Si interface and therefore the effect will be a function of both the path difference in the silicon dioxide layer and the incident wavelength and the effect is larger for both shorter wavelengths and thicker films.

With the reflectance spectra calculated using equation (1), and shown in Fig. 2, differential reflectance spectra are also simulated and relevant examples are shown in figure 3 for the wavelength range 250 nm - 750 nm. For this simulation the thickness of oxide on one sample was fixed at 26 nm while on the other sample the thickness was varied as shown in Fig. 3. These specific thicknesses and wavelength range correspond to some actual ex-situ experimental conditions which will be shown below. In the figure, all spectra can be characterized by two silicon peaks (at about 275 nm and 365 nm), and a gradual increase above 400 nm. The sign of  $\Delta R/R$  is negative in the figure, because the reflectance of a sample with a thinner oxide film (large R) is subtracted from the thicker one (smaller R). Also, the

absolute value of  $\Delta R/R$  increases with large thickness differences between two samples as expected. It should be noted that only the pure interference effect due to a non-absorbing  $\text{SiO}_2$  film has been taken into account in the calculations. Thus, any deviations of experimental  $\Delta R/R$  spectra from the simulations can be attributed to physical and/or chemical phenomena other than interference. Among the many possibilities are two for which precedent exists, namely, the formation of a surface film due to a chemical reaction(5) and/or a possible change of the Si lattice structure due to the release of the film stress by virtue of the etching back the oxide film(17).

### Ex-Situ Differential Reflectance Experiments

The ex-situ experimental results shown in Fig. 4 a and b explore the etching of  $\text{SiO}_2$  films grown on both Si(100) and Si(111) surfaces, respectively, in HF- $\text{H}_2\text{O}$  solutions. Both Si(100) and Si(111) samples were cleaned and oxidized together in order to insure identical experimental conditions. For the Si(100) samples the oxide thickness for the left hand side sample was constant at 25nm, while the other sample was etched back to the values shown in Fig. 4a. In the case of Si(111), the left hand side sample had a fixed thickness of 26nm, while the right hand side was etched back to the values shown in Fig. 4b. In both experiments the thermal oxide was etched completely but the native oxide re grew during the measurement. The simulated spectra corresponding to the ex-situ Si(111) experiments are shown in Fig. 3. and a featureless background spectra is shown in Fig. 4c. The one sample background is obtained from a rastered beam across a single sample and tests the alignment of components

while the two sample background is the centered spectrum taken across two adjacent identical samples, and tests the ability to align the samples.

Firstly, the spectral features in Fig. 4a and b are the same except for the anticipated and predictable intensity differences due to optical interference effects. No Si substrate orientation effect was observed in these experiments, however more detailed studies on this issue are underway and will be reported separately. Secondly, the experimental spectra in Fig. 4 b are very well correlated with the simulated spectra in Fig. 3, showing the same spectral shape with two silicon peaks, a smoothly shaped valley between two peaks, and gradual increase above 400 nm. Any small discrepancy of the absolute value of  $\Delta R/R$  for the equivalent thickness of oxide might be due to the error possibly resulting from the thickness measurement by ellipsometry. In both Fig. 4 a and b, a noticeable broad feature above 650 nm is evident. Since the time that this experiment was performed, the apparatus was improved with the inclusion of a wider bandwidth photomultiplier tube and spectral filters and this feature disappeared as is shown below in the spectra in Figs. 5 and 6. No spectral features are seen in the ex-situ DR spectra that have not been included in the simulations. The great sensitivity of the present DR technique to  $\text{SiO}_2$  thicknesses of less than 3nm is routinely accomplished.

### **In-Situ Differential Reflectance Experiments**

In contrast with the ex-situ experiments above, for the in-situ situation both samples are simultaneously and continuously etched until a bare Si surface is reached, but until this condition is attained there always exists a difference in thickness, since the experiment

commences with different oxide thicknesses. The bottom most spectrum in Fig 5, 1, shows the  $\Delta R/R$  for starting oxide thicknesses of 23.4nm vs. 4nm oxide in deionized water. After replacing the  $H_2O$  with the HF containing etching solution, 400:1 =  $H_2O$ :HF(49%), which had an  $SiO_2$  etch rate of about 4nm/min, the changes in the spectra as a function of time are to be seen by comparing spectra 1 through 8 as shown in Fig. 5.

In all of the spectra shown in Fig. 5 except the initial two at the bottom of the figure which were taken within 10 min of the addition of the etching solution, we estimate that the sample with the initially thinner oxide of 4 nm has reached the Si surface, while for the adjacent sample the oxide is thinning. Firstly, the observed overall decrease of the absolute value of  $\Delta R/R$  with time can be explained by the decreasing thickness difference of the oxides as etching of both samples, being initially thick, proceeds to the Si surface. Secondly, the spectral features for Si near 275nm and 365nm are present as is the overall increase in  $\Delta R/R$  for longer wavelengths as expected, and in concordance with the simulations. However, despite the increased noise for the in-situ measurement, especially at longer wavelengths, the gradual increase in  $\Delta R/R$  as predicted in Fig. 3 and seen for the ex-situ experiments is here in spectra 4 - 7 replaced by a decrease in  $\Delta R/R$  up to about 550nm and then the expected increase. Comparing the top three spectra, 5,6,7 with the bottom spectra, 1 and 2, where the differences in  $SiO_2$  thicknesses are greatest, the broad feature showing a decrease in  $\Delta R/R$  until 550nm is clearly visible. In order to uncover possible artifacts with the in-situ measurement we show in Fig.6 a comparison of in-situ and ex-situ spectra. From these spectra it seems clear that neither the in-situ cell nor liquid in the cell contributes to the decrease in  $\Delta R/R$  above 400nm

although the magnitude of the overall spectra is affected by both the cell and more so by liquid. However, the spectral features are unchanged and the spectra agree with the simulations in Fig. 3. In addition Figure 7 shows that the long time background as well as the fully etched samples spectra show a flat response as anticipated in the region of interest, but the other spectra, 4 through 7 in Fig. 5, shows the decreasing slope in the 400-550nm range. Thus, the broad feature appears to be real.

The broad feature in this 400-550nm region is likely another interference effect associated with a surface film. Evidence for this kind of an effect was presented by Hummel et al for buried layers in ion beam damaged samples(12). While at the present time we are not certain of the origin, we speculate that an electric double layer at the Si surface may be responsible. Under this assumption we explore the consequences of the existence of a double layer adjacent to the Si surface in the solution. First, an electric double layer film would not be observed for the ex-situ experiments. The spectra of Fig. 4 compared with Fig. 5 confirm that the spectral feature is seen only in the in-situ experiments and from Fig. 6 is not an artifact due to the in-situ cell or liquid. Secondly, the optical effects on the in-situ DR spectra can be simulated, viz., the observed decrease in  $\Delta R/R$  in the long wavelength regime. Fig. 8 shows four relevant simulated spectra. Spectra 1 and 2 demonstrate that a transparent film with an index near to that of  $\text{SiO}_2$  cannot cause the spectral feature, nor can a transparent film with a higher index in spectrum 5. Spectra 3 and 4 show that an absorbing film with a higher index yields a decreasing  $\Delta R/R$  in the proper spectral range. For the simulation we chose amorphous Si because R data is available(16), but no implication about the nature of the film is otherwise

implied. The 400-550 nm broad feature is reproduced with the a-Si R data in the DR spectra. but the relative intensities of the higher energy peaks is not reproduced. Before additional simulations are profitable, further information relative to the surface film is required. For the present purpose the postulation of a higher density double layer film is consistent with the observed in-situ spectra. Recently, using in-situ ellipsometry to extend previous work on the etching of  $\text{SiO}_2$  on Si(5), we have uncovered further evidence for the existence of a high index film, only in solution, at or very near the bare Si surface in  $\text{HF}/\text{H}_2\text{O}$  solutions(18). Further work is required to determine the precise nature of the film.

### Conclusions

The differential reflectance technique has been shown to be sensitive to small differences in  $\text{SiO}_2$  film thicknesses on Si substrates. The etching of  $\text{SiO}_2$  can be followed with this technique both ex-situ and in-situ in the  $\text{HF}/\text{H}_2\text{O}$  ambient. Spectral features can be simulated with simple optical models and can provide the bases for interpretation. Some evidence for the existence of a double layer on a bare or nearly bare Si surface is given.

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### Figure Captions

- Figure 1. Block diagram of differential reflectance apparatus.
- Figure 2. Simulation of the reflectivity,  $R$ , from  $\text{SiO}_2$  films of varying thicknesses on a single crystal Si substrate.
- Figure 3. Simulated differential reflectance spectra for two adjacent samples with different  $\text{SiO}_2$  film thickness on Si substrates.
- Figure 4. Ex-Situ experimental results of etching  $\text{SiO}_2$  films in  $\text{HF}/\text{H}_2\text{O}$  solutions: a)  $\text{SiO}_2$  on Si(100), b)  $\text{SiO}_2$  on Si(111) and c) background spectrum.
- Figure 5. In-Situ experimental results of  $\text{SiO}_2$  of 23.4 nm thickness versus 4 nm on (100) Si with 1 the initial spectrum proceeding to 8 at the times indicated on the figure. Background was subtracted from each spectrum.
- Figure 6. A comparison of in-situ and ex-situ spectra with the in-situ spectra in air but in the in-situ cell, 2, and in water in the cell, 1, with ex-situ in air, 3, and all with the same samples of 24nm  $\text{SiO}_2$  versus 4nm both on Si(100) substrates.
- Figure 7. In-situ two sample background spectrum compared with spectrum 7 and 8 from Fig. 5.
- Figure 8. Simulated  $\Delta R/R$  spectrum. Spectra 1 and 2 are a 20nm and 10nm  $\text{SiO}_2$  film adjacent to Si surface, respectively; spectra 3 and 4 are for a 1 and 2 nm a-Si film adjacent to a 5 nm  $\text{SiO}_2$  film on Si surface and a bare Si surface, respectively; and spectrum 5, is for a 2 nm transparent film with an index of 2.0 and a Si surface.

# Differential Reflectometry Apparatus





















